

### REMARKS/ARGUMENTS

Reconsideration is respectfully requested of the Official Action of April 24, 2008, relating to the above-identified application. A one month extension of time, together with the fee associated therewith is filed herein.

Claim 1 has been amended to delete molybdenum from the list of elements (M) forming the mixture of both oxides and sulfides that are contemplated as an active promoter in the manufacture of the methylmercaptan as defined therein. Claims 7 and 8 have been deleted and the features thereof have been introduced into Claim 1.

The number of minor editorial amendments have also been made.

New Claim 41 is based on Claim 1 and defines the active promoter as a cerium oxide, cerium sulfide or cerium oxide and cerium sulfide and, optionally, a carrier.

No new matter is presented.

An extra fee for the additional independent claim is submitted herewith.

The rejection of Claims 1 to 4, 13, 16, 17, and 27 under 35 U.S.C. § 102(a) or (b) in view of the article by Wang, *et al.*, *Ziran Kexueban* (2003), 42(1), 64-68 is traversed and reconsideration is respectfully requested. A complete copy of the article is enclosed herewith as provided by applicants. It will be noted that the reference is completely silent on the use of a promoter which is a mixture of oxides or sulfides or sulfides and oxides of an element (M) where (M) is selected from the group consisting of iron, cobalt, nickel, lanthanum, cerium and manganese.

The cited article of *Wang, et al.*, indicates that the activity of the promoter component decreases from cobalt oxide to nickel oxide to iron oxide. Applicants have determined, as shown by Table 3 in the present application, that the combination of iron and nickel which is catalyst (B) has a higher yield than the use of the cobalt catalyst (A) alone.

Regarding the differences in yield between catalyst (B) and catalyst (A) the MC (Methylmercaptan) yield increases from 0.47 (A) to 0.54 (B). This is an unexpected increase of about 13% related to the desired product. Therefore, the use of catalyst (B) leads to a significant advantage in the commercial use of the invention.

Consequently, applicants submit that an unexpected result has been obtained and discovered by using a mixture of the promoter oxides/sulfides as defined in Claim 1. Accordingly, since the *Wang, et al.*, article does not describe the use of a mixture of the defined elements, applicants respectfully submit that the rejection on the ground of anticipation should be withdrawn.

The rejection of Claims 1 to 4, 13, 16, 17 and 27 under 35 U.S.C. § 102(a) as anticipated by *Yiquan, et al.* (CN 1528516, hereinafter referred to as "CN '516") is traversed and reconsideration is respectfully requested. The CN '516 reference discloses the presence of an active accelerant in combination with the Mo-O-K catalyst where the active accelerator is mainly a transition metal or a rare earth oxide. However, there is no disclosure of the use of a promoter which is a mixture of oxides and/or sulfides of the metals defined in applicants' Claim 1 and,

therefore, applicants respectfully submit that the reference fails to anticipate the claimed invention.

In addition, applicants file herewith a translation of the applicants' three foreign priority documents in order to remove the reference as an effective reference against this application.

The Chinese application 2003101004961 discloses a catalyst and process for synthesis of methylmercaptan from synthesis gas ( $\text{CO} + \text{H}_2$ ) containing a high concentration of hydrogen sulfide. The catalyst includes a solid carrier such as silica and Mo-O-K based complex as an active component. See Claim 1, page 3, lines 9-13.

The Chinese application 2003101004957 discloses a catalyst and process for synthesis in a single step of methylmercaptan from synthesis gas containing high concentration of hydrogen sulfide. The catalyst is Mo-O-K. A promoter is also present which can be a transition metal such as Fe, Mn, Co, Ni, La or Ce; see Claims 1-2. The reaction conditions of elevated temperature and pressure are described on page 6, lines 29, *et seq.*

The Chinese application 2004100083778 discloses a catalyst and process for synthesis of methylmercaptan from synthesis gas containing a high concentration of hydrogen sulfide in the presence of a Mo-O-K active ingredient carrier and one or more promoters including transition metals and/or cerium oxide; see Claim 1.

The rejection of Claims 1 to 4, 13, 16, 17 and 27 under 35 U.S.C. § 102(b) as anticipated by the article authored by Yang, *et al.*, *Catalysis Letters* (2001), Vol. 74, No. 3-4, is traversed and reconsideration is respectfully requested. Yang, *et al.*, do not disclose the use of a mixture of

promoter materials to be used in combination with the main catalyst in accordance with the definition of the process recited in the rejected claims. Consequently, since *Yang, et al.*, do not describe the claimed invention, the reference fails under 35 U.S.C. § 102(b) as an anticipation and applicants respectfully request that the rejection be withdrawn.

The rejection of Claims 5 to 12, 18 to 26, 28 and 30 to 32 under 35 U.S.C. § 103(a) as unpatentable over the *Wang* article (2003), 42(1), 64-68 or *Yiquan, et al.*, CN '516 or the article by *Yang, et al.*, *Catalysis Letters* (2001), further in view of *Buchholz* (GB 2 016 468) is traversed and reconsideration is respectfully requested. None of the main references; namely, *Wang, et al.* (2003) or CN '516 or *Yang (Catalysis Letters)* teaches or suggests the use of a combination of promoter elements as defined in the claims of the present application for the synthesis of methylmercaptan.

The British patent of *Buchholz* does not provide the missing guidelines whereby a person skilled in the art would be led to the combination of components whereby as applicant has demonstrated in Table 3, unexpected improvements are obtained in terms of the yield of the desired product. In fact, applicants' data in Table 3 shows that catalyst (B) which is a combination of iron and nickel oxides, obtains superior results in terms of yield compared with the use of catalyst (A) which uses as a co-catalyst the cobalt material alone. A person skilled in the art could not have predicted the unexpected results in terms of improved yield when using a mixture of materials as a promoter. Therefore, applicants respectfully submit that the record

herein shows that unexpected results are obtained and, accordingly, the rejection in terms of obviousness of the claimed invention should be withdrawn.

Favorable action at the Examiner's earliest convenience is respectfully requested.

Respectfully submitted,

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UNITED STATES PATENT AND TRADEMARK OFFICE

I, Charles Edward SITCH BA,

Managing Director of RWS Group Ltd UK Translation Division, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That the translator responsible for the attached translation is well acquainted with the Chinese and English languages.
3. That the attached is, to the best of RWS Group Ltd knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in China on March 12, 2004 under the number 2004100083778 and the official certificate attached thereto.
4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.

  
For and on behalf of RWS Group Ltd

The 7th day of July 2008

11 November 2004

**CERTIFICATE**

The appendix to this certificate is a copy of the following patent application submitted to this office

Received 06 December 2004

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Date of filing: 12.03.2004

Application No.: 2004100083778

Type of application: invention

Title of invention / creation: A catalyst for the synthesis of methyl mercaptan through the reaction of carbon monoxide with hydrogen sulphide

Applicant: Xiamen University

Inventors or designers: Yang Yiquan, Wang Qi, Dai Shenjun, Yan Xingguo, Chen Aiping, Zheng Quanxing, Fang Weiping, Yuan Youzhu, Zhang Hongbin

**Priority**

Document

Submitted or transmitted in compliance  
with Rule 17.1 (a) or (b)

Commissioner of the State Intellectual Property Office  
of the People's Republic of China: Wang Jingchuan

11 October 2004

Claims

1. Catalyst for the synthesis of methyl mercaptan through the reaction of carbon monoxide with hydrogen sulphide, characterized in that the said catalyst comprises an active ingredient, promoter and carrier, the said active ingredient being an Mo-O-K based complex, the promoter being at least one oxide of a transitional metal and/or cerium oxide, and the carrier being  $\text{SiO}_2$ ; the said active ingredient Mo-O-K based complex is obtained by the conversion of the precursor  $\text{K}_2\text{MoO}_4$  and is calculated as  $\text{K}_2\text{MoO}_4$  or is converted from  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  plus a potassium salt and is calculated as  $\text{MoO}_3 + \text{K}_2\text{O}$ , while the transitional metal oxide and cerium oxide promoter is calculated by mass as  $\text{Mo}_x$ ; the proportions by weight of the various components in the catalyst are  $\text{K}_2\text{MoO}_4 / \text{Mo}_x / \text{carrier} = (0.05-0.80) / (0.01-0.10) / 1$  or  $\text{MoO}_3 / \text{K}_2\text{O} / \text{Mo}_x / \text{carrier} = (0.10-0.50) / (0.10-0.30) / (0.01-0.10) / 1$ ; before use, the catalyst is first reduced using  $\text{H}_2$  or  $\text{H}_2 + \text{CO}$  gas at  $300-350^\circ\text{C}$  for 8 h, and the usage conditions for the catalyst are: volumetric proportions of the components in the feed gas  $\text{CO} : \text{H}_2\text{S} = 1 / (3-0.1)$ , reaction temperature  $220-350^\circ\text{C}$ , pressure 0.1-2.0 MPa, reaction gas volumetric spatial velocity  $(2-5) \times 10^3 \text{h}^{-1}$ .

2. Catalyst for the synthesis of methyl mercaptan through the reaction of carbon monoxide with hydrogen sulphide according to Claim 1, characterized in that the said potassium salt is selected from KOH,  $\text{K}_2\text{CO}_3$ ,  $\text{KAC}$ ,  $\text{K}_2\text{C}_2\text{O}_4$  or  $\text{KNO}_3$ .

3. Catalyst for the synthesis of methyl mercaptan through the reaction of carbon monoxide with hydrogen sulphide according to Claim 1, characterized in that the said transitional metal oxide is the oxide of Fe, Co, Ni or Mn.

4. Catalyst for the synthesis of methyl mercaptan through the reaction of carbon monoxide with hydrogen sulphide according to Claims 1 and 3, characterized in that the precursor of the said transitional metal oxide  
5 or cerium oxide is the respective nitrate or acetate.

5. Catalyst for the synthesis of methyl mercaptan through the reaction of carbon monoxide with hydrogen sulphide according to Claim 1, characterized in that  
10 the proportions by mass of the components of the catalyst are  $K_2MoO_4 / MO_x / \text{carrier} = (0.1-0.5) / (0.01-0.06) / 1$  or  $MoO_3 / K_2O / MO_x / \text{carrier} = (0.10-0.30) / (0.10-0.25) / (0.01-0.06) / 1$ .

15 6. Catalyst for the synthesis of methyl mercaptan through the reaction of carbon monoxide with hydrogen sulphide according to Claim 1, characterized in that the proportions by volume of the components in the feed gas are  $CO : H_2S = 1 / (3-1)$ .

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7. Method of preparing the catalyst for the synthesis of methyl mercaptan through the reaction of carbon monoxide with hydrogen sulphide, characterized in that the preparation of the said catalyst is by a step-by-step soaking method:  
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(1) A measured amount of carrier is soaked in a measured amount of an aqueous solution of a soluble salt of the selected transitional metal and/or Ce for a  
30 soaking time of 4-6 h, followed by heat drying at 100-135°C for 2-4 h and finally calcination at 500-600°C for 4-6 h, to form an intermediate modified by the transitional metal oxide and/or cerium oxide;

35 (2) When the active ingredient precursor is  $K_2MoO_4$ , the intermediate prepared by modification with the transitional metal oxide and/or cerium oxide from step (1) is soaked in a measured amount of  $K_2MoO_4$  aqueous solution according to the formulation proportions of

the catalyst for a soaking time of 4-6 h, followed by heat drying at 110-130°C for 2-4 h and finally calcination at 400-550°C for 3-5 h; when the active ingredient precursor is  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  plus a potassium salt, the intermediate prepared by the modification by the transitional metal oxide and/or cerium oxide from step (1) is soaked in a measured amount of a potassium salt solution according to the formulation proportions of the catalyst for a soaking time of 4-6 h, followed by heat drying at 100-130°C for 2-4 h, after which the carrier modified by the transitional metal oxide and/or cerium oxide and potassium salt is soaked in a measured amount of an aqueous solution of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  according to the formulation proportions of the catalyst for a soaking time of 5-8 h, followed by heat drying at 110-130°C for 2-4 h and finally calcination at 400-550°C for 3-5 h.

**Description**

A Catalyst for the Synthesis of Methyl Mercaptan  
through the Reaction of Carbon Monoxide with Hydrogen  
Sulphide

**Technical Field**

This invention relates to a catalyst for the synthesis of methyl mercaptan by a reaction of carbon monoxide (CO) with hydrogen sulphide (H<sub>2</sub>S). The said catalyst is a supported Mo-O-K based complex system with at least one transitional metal oxide and/or cerium oxide as promoter.

**Prior Art**

Methyl mercaptan is a major chemical engineering intermediate used for the synthesis of protein amino acids, medical drugs and agrochemicals. Existing technical routes for the synthesis of methyl mercaptan include: a route for the synthesis of methyl mercaptan from the reaction of methanol with hydrogen sulphide disclosed in American patents US 5977011 and US 6198003, European patents EP 0564706A and EP 1005906, Japanese laid-Open patent JP 219673 (2000), the main catalyst system being WO<sub>3</sub>-K<sub>2</sub>O /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MgO + ZrO /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; a route for the direct synthesis of methyl mercaptan from H<sub>2</sub>S and synthesis gas (CO + H<sub>2</sub>) as starting materials as disclosed in Chinese patents ZL 98118186.4 and ZL 98118187.2, the catalyst for which was a supported Mo-S-K based complex catalyst, characterized by a relatively high methyl mercaptan selectivity and space time yield; and a scheme for the direct synthesis of methyl mercaptan from carbon monoxide and hydrogen sulphide as disclosed in American patents US 4668825 and US 4570020, the catalyst system used being a catalyst of V, Nb and Ta oxides supported

on a  $\text{TiO}_2$  carrier, this catalyst system giving a maximum CO conversion rate of 36% at  $300^\circ\text{C}$ .

### Scope of Invention

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The objective of this invention is to provide a new catalyst system for the direct synthesis of methyl mercaptan from carbon monoxide and hydrogen sulphide. This catalyst system is a supported Mo-O-K based complex system with at least one oxide of a transitional metal and/or cerium oxide as promoter.

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The said catalyst of this invention is a catalyst system for the direct synthesis of methyl mercaptan from carbon monoxide and hydrogen sulphide, comprising an active ingredient, promoter and carrier, the said active ingredient being an Mo-O-K based complex, the promoter being at least one oxide of a transitional metal and/or cerium oxide ( $\text{CeO}_2$ ), and the carrier being  $\text{SiO}_2$ . The said active ingredient Mo-O-K based complex can be obtained by the conversion of the precursor  $\text{K}_2\text{MoO}_4$  and is calculated as  $\text{K}_2\text{MoO}_4$ , or is converted from  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  plus a potassium salt and is calculated as  $\text{MoO}_3 + \text{K}_2\text{O}$ , the said potassium salt being selected from KOH,  $\text{K}_2\text{CO}_3$ , KAc,  $\text{K}_2\text{C}_2\text{O}_4$  or  $\text{KNO}_3$ ; the said transitional metal oxide is the oxide of Fe, Co, Ni or Mn, and the precursor of the transitional metal oxide or cerium oxide is the respective nitrate or acetate; the oxide promoter is calculated as  $\text{MO}_x$  (weight), and if there is more than one oxide,  $\text{MO}_x$  represents the total of the various oxides. The proportions by weight of the various components in the catalyst are  $\text{K}_2\text{MoO}_4 / \text{MO}_x / \text{carrier} = (0.05-0.80) / (0.01-0.10) / 1$  and preferably  $(0.1-0.5) / (0.01-0.06) / 1$  or  $\text{MoO}_3 / \text{K}_2\text{O} / \text{MO}_x / \text{carrier} = (0.10-0.50) / (0.10-0.30) / (0.01-0.10) / 1$  and preferably  $(0.10-0.30) / (0.10-0.25) / (0.01-0.06) / 1$ .

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Preparation of the catalyst is by a step-by-step soaking method as follows:

(1) A measured amount of the selected transitional metal and/or Ce soluble salt is dissolved in a fixed volume of distilled water to form an aqueous solution of a certain concentration, but it is also possible to measure out a certain volume of a solution of a transitional metal and/or Ce soluble salt of known concentration, and this solution is then used to soak a measured amount of carrier; if the promoter is not limited to one kind, the separate aqueous solutions should first be made up and then combined to form a mixed aqueous solution, which is then used for soaking a measured amount of the carrier for a soaking time of 4-6 h, followed by heat drying at 100-135°C for 2-4 h and finally calcination at 500-600°C for 4-6 h, to form an intermediate modified by the transitional metal oxide and/or cerium oxide.

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(2) When the active ingredient precursor is  $K_2MoO_4$ , a measured amount of  $K_2MoO_4$  is dissolved in a measured volume of distilled water to form an aqueous solution of  $K_2MoO_4$  of a certain concentration, and this solution is then used to soak the carrier prepared in step (1) and modified by the transitional metal oxide and/or cerium oxide for a soaking time of 5-8 h, followed by heat drying at 110-130°C for 2-4 h and finally calcination at 400-550°C for 3-5 h;

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When the active ingredient precursor is  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  plus a potassium salt, a measured amount of the selected potassium salt is first dissolved in a certain volume of distilled water to form a potassium salt solution of a certain concentration, and this solution is then used to soak the carrier prepared in step (1) and modified by the transitional metal oxide and/or cerium oxide for a soaking time of 4-6 h, followed by heat drying at 100-130°C for 2-4 h; the same method is

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used to dissolve a measured amount of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in a certain volume of distilled water to form an aqueous solution of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  of a certain concentration, and this solution is then used to soak the carrier modified by the transitional metal oxide and/or cerium oxide and the potassium salt for a soaking time of 5-8 h, followed by heat drying at 110-130°C for 2-4 h, and finally calcination at 400-550°C for 3-5 h.

Before use, the catalyst must first be reduced using  $\text{H}_2$  or  $\text{H}_2 + \text{CO}$  gas for 8 h at 300-350°C. The conditions for using the catalyst of this invention are: proportions by volume of the various components of the feed gas  $\text{CO} : \text{H}_2\text{S} = 1 / (3-0.1)$  and preferably  $1 / (3-1)$ , reaction temperature 220-350°C, pressure 0.1-2.0 MPa, and volumetric spatial velocity of reaction gas (GHSV)  $(2-5) \times 10^3 \text{h}^{-1}$ .

This invention was assessed in a fixed bed tubular fluid reaction system. The feed gas and reaction products were analysed by gas chromatography, and samples were analysed 2 h after the reaction had reached a stable state. This invention has a very high activity and selectivity in the formation of methyl mercaptan, and under the assessment conditions for this invention, the CO conversion rate was 45% - 90%, the methyl mercaptan space time yield was  $0.8 \text{ g.h}^{-1} \cdot \text{ml}^{-1}_{\text{cat}}$ , and the selectivity reached 99%.

#### Embodiments

This invention is further described below through practical examples.

#### Practical Example 1

10.0 g of  $\text{SiO}_2$  (grade 80-100) were soaked in 20 ml of an aqueous solution of  $\text{Fe}(\text{NO}_3)_3$  with a concentration of

0.25 M for 4 h and this was then heat dried at 110°C for 3 h and calcined at 550°C for 4 h, to form an  $\text{Fe}_2\text{O}_3$  /  $\text{SiO}_2$  intermediate; 5.025 g of  $\text{K}_2\text{MoO}_4$  were dissolved in 20 ml of distilled water to form an aqueous solution which was then used to soak the prepared  $\text{Fe}_2\text{O}_3$  /  $\text{SiO}_2$  intermediate for 8 h, followed by heat drying at 110°C for 3 h and calcination at 500°C for 4 h; the proportions by weight of the various components of the catalyst were  $\text{K}_2\text{MoO}_4$  /  $\text{Fe}_2\text{O}_3$  /  $\text{SiO}_2$  = 0.5 / 0.04 / 1.

#### Practical Example 2

0.5 g of the catalyst prepared in Practical Example 1 was placed in a stainless steel tubular reactor and was reduced with  $\text{H}_2$  at 350°C for 8 h, after which the feed gas was introduced to conduct the reaction, the proportions by volume of the various components of the feed gas being  $\text{CO} : \text{H}_2\text{S} = 1 / 1$ ; reaction temperature: 295°C; pressure: 0.2 MPa; spatial velocity:  $3 \times 10^3 \text{h}^{-1}$ . A sample was taken 2 h after the reaction had reached a stable state and was analysed by chromatography. See Table 1 (column A) for the analytical results.

#### Practical Example 3

0.5 g of the catalyst prepared in Practical Example 1 was placed in a stainless steel tubular reactor and was reduced with  $\text{H}_2$  at 330°C for 8 h, after which the feed gas was introduced to conduct the reaction, the proportions by volume of the various components of the feed gas being  $\text{CO} : \text{H}_2\text{S} = 1 / 3$ ; reaction temperature: 300°C; pressure: 0.6 MPa; spatial velocity:  $3 \times 10^3 \text{h}^{-1}$ . A sample was taken 2 h after the reaction had reached a stable state and was analysed by chromatography. See Table 1 (column B) for the analytical results.

#### Practical Example 4

"18 ml of 0.20M  $\text{Mn}(\text{NO}_3)_2$  solution" replaced the "20 ml of an aqueous solution of  $\text{Fe}(\text{NO}_3)_3$  with a concentration of 0.25M" in Practical Example 1, while the remainder of the method was as in Practical Example 1. 0.5 g of the catalyst thus prepared was assessed by the method in Practical Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 1.

#### Practical Examples 5-7

The "20 ml of an aqueous solution of  $\text{Fe}(\text{NO}_3)_3$  with a concentration of 0.25M" in Practical Example 1 was changed to taking 1.20 g of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 1.20 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.65 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  respectively and dissolving each in 20 ml of distilled water. These were combined to form mixed solutions, while the remainder of the preparation method was the same as the steps in Practical Example 1. 0.5 g of the catalyst thus prepared was assessed by the method in Practical Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 1.

#### Practical Example 8

0.500 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 15 ml of distilled water to form an aqueous solution of  $\text{Ce}(\text{NO}_3)_3$ , and this was combined with 10 ml of a 0.5M  $\text{Fe}(\text{NO}_3)_3$  aqueous solution to form a mixed solution, while the remainder of the method was the same as the steps in Practical Example 1. 0.5 g of the catalyst thus prepared was assessed by the method in Practical Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 1.

### Practical Example 9

A solution made up by dissolving 1.250 g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 10 ml of distilled water was combined  
5 with a solution made up by dissolving 0.500 g of  $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$  in 15 ml of distilled water, and this solution was used to soak 10.0 g of  $\text{SiO}_2$  for 5 h, followed by heat drying at  $110^\circ\text{C}$  for 4 h and calcination at  $550^\circ\text{C}$  for 4 h to form an  $\text{Fe}_2\text{O}_3$  /  $\text{NiO}$  /  
10  $\text{SiO}_2$  intermediate, which was in turn soaked in a solution of 2.505 g of  $\text{K}_2\text{MoO}_4$  dissolved in 20 ml of distilled water for 6 h, followed by heat drying at  $120^\circ\text{C}$  for 3 h and calcination at  $500^\circ\text{C}$  for 4 h. 0.5 g of the catalyst thus prepared was assessed by the  
15 method in Practical Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 1.

### Practical Example 10

20 The  $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$  in Practical Example 9 was changed to  $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ , while the remainder was the same as in Practical Example 9. 0.5 g of the catalyst thus prepared was assessed by the method in Practical  
25 Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 1.

### Practical Example 11

30 10 ml of a solution of  $\text{Fe}(\text{NO}_3)_3$  with a concentration of 0.25M were diluted with 10 ml of distilled water to form an aqueous solution of ferric nitrate with a different concentration, and this solution was then  
35 used to soak 10.0 g of  $\text{SiO}_2$  (grade 80 to 100) for 4 h, and this was heat dried at  $110^\circ\text{C}$  for 3 h and then calcined at  $550^\circ\text{C}$  in a muffle furnace for 4 h to form an  $\text{Fe}_2\text{O}_3$  /  $\text{SiO}_2$  intermediate; the  $\text{Fe}_2\text{O}_3$  /  $\text{SiO}_2$  intermediate prepared in the previous step was soaked

in an aqueous solution of 3.50 g of  $K_2CO_3$  dissolved in 20 ml of distilled water for 4 h, followed by heat drying at  $120^\circ C$  for 4 h until ready for use; the next step involved soaking the  $Fe_2O_3$  /  $K_2CO_3$  /  $SiO_2$  intermediate modified in the previous two steps by  $Fe_2O_3$  and  $K_2CO_3$  in an aqueous solution prepared by dissolving 3.71 g of  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  in 25 ml of distilled water for 7 h, followed by heat drying at  $110^\circ C$  for 4 h and calcination at  $500^\circ C$  for 3 h. 0.5 g of the catalyst thus prepared was assessed by the method in Practical Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 2.

#### 15 Practical Examples 12-14

The  $K_2CO_3$  in Practical Example 11 was changed to 2.52 g of KOH, 3.08 g of KAc and 3.64 g of  $K_2C_2O_4$  respectively. The remaining steps and method were the same as in Practical Example 11. 0.5 g of the catalyst thus prepared was assessed by the method in Practical Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 2.

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#### Practical Example 15

0.500 g of  $Ce(NO_3)_3 \cdot 6H_2O$  was dissolved in 15 ml of distilled water to form an aqueous solution of  $Ce(NO_3)_3$ , which was then combined with 5 ml of a 0.5M aqueous solution of  $Fe(NO_3)_3$  to form a mixed solution, and 10.0 g of  $SiO_2$  (grade 80-100) were soaked in the solution for 4 h, heat dried at  $110^\circ C$  for 3 h and then calcined in a muffle furnace at  $550^\circ C$  for 4 h to form an  $Fe_2O_3$  /  $CeO_2$  /  $SiO_2$  intermediate; this intermediate was then soaked for 4 h in an aqueous solution of 2.50 g of  $K_2CO_3$  dissolved in 20 ml of distilled water, followed by heat drying at  $120^\circ C$  until ready for use; the next step involved soaking the  $Fe_2O_3$  /  $CeO_2$  /  $K_2CO_3$  /

SiO<sub>2</sub> carrier modified by Fe<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and K<sub>2</sub>CO<sub>3</sub> in the previous two steps for 8 h in an aqueous solution made by dissolving 2.28 g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> · 4H<sub>2</sub>O in 25 ml of distilled water, followed by heat drying at 130°C for 2 h and calcination at 500°C for 3 h. 0.5 g of the catalyst thus prepared was assessed by the method in Practical Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 2.

#### Practical Examples 16 and 17

The 0.500 g of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O in Practical Example 15 was changed to 0.500 g of Ni(Ac)<sub>2</sub>·4H<sub>2</sub>O and 0.500 g of Co(Ac)<sub>2</sub>·4H<sub>2</sub>O respectively, while the remaining steps and method were the same as in Practical Example 15. 0.5 g of the catalyst thus prepared was assessed by the method in Practical Examples 2 and 3, and the composition and activity assessment results of the catalyst are shown in Table 2.

Table 1. Compositions and Activity Assessment Results of the Catalysts in Practical Examples 1-10

Practical Example	Catalyst composition (active ingredient calculated as K <sub>2</sub> MoO <sub>4</sub> )	CO conversion rate %		CH <sub>3</sub> SH selectivity %***		CH <sub>3</sub> SH space-time yield (g·h <sup>-1</sup> ·ml <sup>-1</sup> ·cat)	
		A *	B **	A *	B **	A *	B **
1	K <sub>2</sub> MoO <sub>4</sub> /Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> = 0.5/0.04/1	59.0	71.5	99.0	99.3	0.52	0.68
4	K <sub>2</sub> MoO <sub>4</sub> /MnO <sub>2</sub> /SiO <sub>2</sub> = 0.5/0.03/1	45.8	48.6	97.3	98.5	0.42	0.45
5	K <sub>2</sub> MoO <sub>4</sub> /NiO/SiO <sub>2</sub> = 0.5/0.031/1	72	86.5	99.1	99.6	0.71	0.80
6	K <sub>2</sub> MoO <sub>4</sub> /CoO/SiO <sub>2</sub> = 0.5/0.031/1	67	87	99.4	99.7	0.63	0.80
7	K <sub>2</sub> MoO <sub>4</sub> /CeO <sub>2</sub> /SiO <sub>2</sub> = 0.5/0.025/1	50	68	99.0	99.3	0.47	0.51
8	K <sub>2</sub> MoO <sub>4</sub> /CeO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> = 0.5/0.02/0.02/1	59.2	72	99.1	99.4	0.53	0.69
9	K <sub>2</sub> MoO <sub>4</sub> /NiO /Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> = 0.25/0.03/0.015/1	68	90	99.2	99.5	0.65	0.84
10	K <sub>2</sub> MoO <sub>4</sub> /CoO /Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> = 0.25/0.03/0.015/1	67	88	99.0	99.3	0.64	0.81

Table 2. Compositions and Activity Assessment Results  
of the Catalysts in Practical Examples 11-17

Practical Example	Catalyst composition (active ingredient calculated as MoO <sub>3</sub> and K <sub>2</sub> O)	CO conversion rate %		CH <sub>3</sub> SH selectivity %***		CH <sub>3</sub> SH space-time yield (g h <sup>-1</sup> ml <sup>-1</sup> cat)	
		A *	B **	A *	B **	A *	B **
11	MoO <sub>3</sub> /K <sub>2</sub> O/Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> = 0.3/0.21/0.02/1	55.0	65.2	98.0	98.4	0.45	0.55
12	MoO <sub>3</sub> /K <sub>2</sub> O/Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> = 0.3/0.21/0.02/1	56.3	66.0	99.0	99.2	0.46	0.57
13	MoO <sub>3</sub> /K <sub>2</sub> O/Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> = 0.3/0.21/0.02/1	45.6	50.7	90.0	92.1	0.38	0.41
14	MoO <sub>3</sub> /K <sub>2</sub> O/Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> = 0.3/0.21/0.02/1	49.0	50.2	93.3	94.2	0.45	0.50
15	MoO <sub>3</sub> /K <sub>2</sub> O/Fe <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /SiO <sub>2</sub> = 0.18/0.17/0.02/0.02/1	50.0	65.0	98.1	98.6	0.46	0.57
16	MoO <sub>3</sub> /K <sub>2</sub> O/Fe <sub>2</sub> O <sub>3</sub> /NiO/SiO <sub>2</sub> = 0.18/0.17/0.02/0.015/1	58.5	68.2	98.3	98.9	0.51	0.59
17	MoO <sub>3</sub> /K <sub>2</sub> O/Fe <sub>2</sub> O <sub>3</sub> /CoO/SiO <sub>2</sub> = 0.18/0.17/0.02/0.015/1	57.3	65.5	98.1	98.7	0.50	0.57

5 \* Assessment results under the assessment conditions of Practical Example 2

\*\* Assessment results under the assessment conditions of Practical Example 3

\*\*\* CO<sub>2</sub> not counted in selectivity

UNITED STATES PATENT AND TRADEMARK OFFICE

I, Charles Edward SITCH BA,

Managing Director of RWS Group Ltd UK Translation Division, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That the translator responsible for the attached translation is well acquainted with the Chinese and English languages.
3. That the attached is, to the best of RWS Group Ltd knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in China on October 10, 2003 under the number 2003101004957 and the official certificate attached thereto.
4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.



For and on behalf of RWS Group Ltd

The 7th day of July 2008

11 November 2004

**CERTIFICATE**

The appendix to this certificate is a copy of the following  
patent application submitted to this office

Received 06 December 2004

WIPO PCT

Date of filing: 10.10.2003

Application No.: 2003101004957

Type of application: invention

Title of invention/creation: a catalyst for the single-step  
preparation of methyl mercaptan from synthesis gas containing  
a high concentration of hydrogen sulphide

Applicant: Xiamen University

Inventors or designers: Yang Yiquan, Wang Qi, Lin Rencun,  
Zhang Hongbin, Yuan Youzhu, Fang Weiping, Zheng Quanxing, Dai  
Shenjun, Yan Xingguo

**Priority**

Document

Submitted or transmitted in compliance  
with Rule 17.1 (a) or (b)

Commissioner of the State Intellectual Property Office of the  
People's Republic of China: Wang Jingchuan

11 October 2004

Claims

1. A catalyst for the single-step preparation of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide, the catalyst being composed of an active component, active promoter and carrier, characterized in that the said active component is a Mo-O-K based complex, its precursor being potassium molybdate (active component calculated on the basis of  $K_2MoO_4$ ) or ammonium molybdate plus potassium salt or molybdenum oxide with the addition of a potassium salt (active component calculated on the basis of  $MoO_3$  and  $K_2O$ ); the active promoter is an oxide selected from that of a transitional metal or lanthanum series rare earth element with measurement expressed as  $MO_x$ , and the carrier is selected from silica or titanium oxide; the proportions by weight of the components making up the catalyst calculated on the basis of  $K_2MoO_4$  as the active component are  $K_2MoO_4 / MO_x / \text{carrier} = (0.01-0.80) / (0.001-0.01) / 1$ , and the proportions by weight of the components making up the catalyst calculated on the basis of  $MoO_3$  and  $K_2O$  as the active component are  $MoO_3 / K_2O / MO_x / \text{carrier} = (0.10-0.50) / (0.10-0.30) / (0.01-0.10) / 1$ .
2. Catalyst for the single-step preparation of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide according to Claim 1, characterized in that the said transitional metal or lanthanum series rare earth element oxide is the oxide of iron, manganese, cobalt, nickel, lanthanum or cerium.
3. Catalyst for the single-step preparation of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide according to Claim 1, characterized in that the proportions by weight of the components making up the catalyst calculated on

the basis of  $K_2MoO_4$  as the active component are  $K_2MoO_4$  /  $MO_x$  / carrier = (0.10-0.60) / (0.01-0.06) / 1.

4. Catalyst for the single-step preparation of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide according to Claim 1, characterized in that the proportions by weight of the components making up the catalyst calculated on the basis of  $MoO_3$  and  $K_2O$  as the active component are  $MoO_3$  /  $K_2O$  /  $MO_x$  / carrier = (0.10-0.30) / (0.10-0.25) / (0.01-0.06) / 1.

5. Preparation method for a catalyst for the single-step preparation of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide, characterized in that the steps are as follows:

1) A nitrate of the selected transitional metal or lanthanum series rare earth element is weighed out and dissolved in distilled water to form a solution, which is then used for soaking a measured amount of the selected carrier for 3-5 h, and this is then heat-dried at 100-130°C for 1-3 h ready for use;

2) The selected active component precursor  $K_2MoO_4$  or  $(NH_4)_6Mo_7O_{24}$  plus a potassium salt or  $MoO_3$  plus a potassium salt are weighed out, and after dissolving in distilled water are used to soak the carrier modified as in step (1) for 7-9 h, which is heat-dried at 100-130°C and calcined at 400-500°C for 2-4 h.

6. Preparation method for a catalyst for the single-step preparation of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide according to Claim 5, characterized in that the catalyst preparation method used when the precursor of the active component is  $(NH_4)_6Mo_7O_{24}$  and a potassium salt is a multi-step soaking process for step 2, namely first dissolving the measured potassium salt in

distilled water and using it to soak the carrier modified by a metallic oxide for 1-3 h and heat-drying at 100-130°C, followed by dissolving a measured amount of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  in distilled water and then using this to  
5    soak the carrier modified by the potassium salt for 7-9 h, heat-drying at 100-130°C and calcining at 400-500°C for 2-4 h.

Description

Catalyst for the Single-Step Preparation of Methyl  
Mercaptan from Synthesis Gas Containing a High  
Concentration of Hydrogen Sulphide

(1) Technical Field

This invention relates to a supported catalyst used for the single-step synthesis of methyl mercaptan ( $\text{CH}_3\text{SH}$ ) from synthesis gas ( $\text{CO} + \text{H}_2$ ) with a high concentration of  $\text{H}_2\text{S}$  as the starting material, and a method for its preparation.

(2) Prior Art

Methyl mercaptan is an important chemical engineering starting material for synthesizing protein amino acids, medical drugs and agrochemicals, and the traditional method for its manufacture is through the action of potassium hydrosulphide on a halogenated methane. Other synthesis routes have subsequently been developed, such as American patent US appl. 856,232, which disclosed a reaction of hydrogen sulphide with methanol or ethyl ether to form methyl mercaptan; French patent FR appl. 93,112,491, which disclosed a method involving the hydrogenation of methylthioether for the preparation of methyl mercaptan using a transitional metal as catalyst; European patent EP 167,354, which disclosed a method for the preparation of methyl mercaptan using hydrogen sulphide and carbon monoxide as the starting material and with titanium oxide as the carrier and nickel oxide or molybdenum oxide as the active component. Chinese patents ZL 98118186.4 and ZL 98118187.2 disclosed a catalyst for the manufacture of methyl mercaptan from a synthesis gas containing a high concentration of  $\text{H}_2\text{S}$ , the active component being an Mo-S-K group produced by the conversion of a precursor  $\text{K}_2\text{MoS}_4$  or  $(\text{NH}_4)_2\text{MoS}_4$  plus a potassium salt. The space-

time yield of methyl mercaptan with this catalyst was relatively low ( $0.08-0.19 \text{ g} \cdot \text{h}^{-1} \cdot \text{ml}^{-1}_{\text{cat}}$ ), the preparation of the precursor was also very difficult, and water could not be used as the carrier solvent, requiring the use of DMF, so that the manufacturing cost of the catalyst was high.

### (3) Scope of Invention

The objective of this invention is to provide a catalyst for the single-step preparation of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide as starting material and which features cheap starting materials, simple preparation, a high methyl mercaptan space-time yield and relatively high activity and selectivity.

The catalyst of this invention comprises an active component, active promoter and carrier. The active component is a  $\text{Mo-O-K}$  based complex, its precursor being potassium molybdate (active component calculated as  $\text{K}_2\text{MoO}_4$ ) or ammonium molybdate  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}]$  plus a potassium salt or molybdenum oxide ( $\text{MoO}_3$ ) plus a potassium salt (active component calculated as  $\text{MoO}_3$  and  $\text{K}_2\text{O}$ ); the active promoter is an oxide selected from that of a transitional metal or lanthanum series rare earth element and in particular iron (Fe), manganese (Mn), cobalt (Co), nickel (Ni), lanthanum (La) or cerium (Ce) oxide with the amount expressed as  $\text{MO}_x$ ; the carrier is selected from silica ( $\text{SiO}_2$ ) or titanium oxide ( $\text{TiO}_2$ ); the proportions by weight of the components making up the catalyst calculated on the basis of  $\text{K}_2\text{MoO}_4$  as the active component are  $\text{K}_2\text{MoO}_4 / \text{MO}_x / \text{carrier} = (0.01-0.80) / (0.001-0.01) / 1$ , and preferably  $(0.10-0.60) / (0.01-0.06) / 1$ ; and if calculated with  $\text{MoO}_3$  and  $\text{K}_2\text{O}$  as the active component, the proportions by weight in the catalyst are  $\text{MoO}_3 / \text{K}_2\text{O} / \text{MO}_x / \text{carrier} = (0.10-0.50) / (0.10-0.30) / (0.01-0.10) / 1$ , and preferably  $(0.10-0.30) / (0.10-0.25) / (0.01-0.06) / 1$ .

The preparation method for the catalyst is as follows:

- 1) A nitrate of the selected transitional metal or lanthanum series rare earth element is weighed out and dissolved in distilled water to form a solution, which is then used for soaking a measured amount of the selected carrier for 3-5 h, and this is then heat-dried at 100-130°C for 1-3 h ready for use;
- 2) The selected active component precursor ( $K_2MoO_4$  or  $(NH_4)_6Mo_7O_{24}$  plus a potassium salt or  $MoO_3$  plus a potassium salt) is weighed out, and after dissolving in distilled water is used to soak the carrier modified as in step (1) for 7-9 h, which is heat-dried at 100-130°C and calcined at 400-500°C for 2-4 h.

A multi-step soaking method can also be used when the active component precursor is  $(NH_4)_6Mo_7O_{24}$  and a potassium salt, namely by first dissolving the measured potassium salt in distilled water and using it to soak the carrier modified by a metallic oxide for 1-3 h and heat-drying at 100-130°C, followed by dissolving a measured amount of  $(NH_4)_6Mo_7O_{24}$  in distilled water and then using this to soak the carrier modified by the potassium salt for 7-9 h, heat-drying at 100-130°C and calcining at 400-500°C for 2-4 h.

Assessment of catalyst activity is carried out in a fluid reaction system on a fixed bed, with the composition of the starting material gas being (proportions by volume)  $CO/H_2/H_2S = 1/2/(0.1-1)$ , the reaction temperature 220-350°C, the pressure 0.1-2.0 MPa, spatial velocity  $(2-5) \times 10^3 h^{-1}$ . The compositions of the starting material gas and product are determined by gas chromatography. The catalyst is first reduced for 8 h by  $H_2$  at 300-350°C, after which starting material gas is passed in for 8 h followed by measurement of product composition.

As is generally known, the properties and performance of a catalyst are determined by the starting materials for its manufacture and the manufacturing method (including process conditions). When the catalyst contains a certain element, for example Mo, it is in principle possible to select all simple substances or compounds containing the element Mo as one of the starting materials for manufacture of this catalyst. However, different starting materials inevitably introduce other different groups or atoms, so that when selecting  $\text{MoO}_3$ , O atoms are introduced, while when selecting ammonium molybdate, O atoms and  $\text{NH}_4^+$  groups are introduced. These other introduced groups will affect the physical changes and chemical changes which occur during the catalyst manufacturing process, and thus finally result in differences in the properties and performance of the catalyst. This invention prepares a catalyst with high activity and selectivity through the selection of appropriate starting materials containing Mo and K, and under the assessment conditions of this invention, the space-time yield of methyl mercaptan was  $0.27\text{--}0.33 \text{ g}\cdot\text{h}^{-1}\cdot\text{ml}^{-1}_{\text{cat}}$ , and selectivity reached 92.7% - 98.6%. Furthermore, the selected starting materials are cheap and readily obtainable, and the manufacturing process is simple and convenient.

#### (4) Embodiments

This invention is further described below by means of practical examples.

Practical Example 1. 0.725 g of  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  was weighed out and dissolved in 20 ml of distilled water to make up a ferric nitrate solution, which was used to soak 10.0 g of  $\text{SiO}_2$  (grade 80-100) for 4 h, and this was heat-dried at  $110^\circ\text{C}$  for 2 h. It was then calcined in a muffle furnace at  $500^\circ\text{C}$  for 4 h and cooled ready for

use. 5.0 g of  $K_2MoO_4$  was weighed out and dissolved in 20 ml of distilled water to form an aqueous solution of  $K_2MoO_4$ , which was used to soak 10 g of  $SiO_2$  modified with Fe as described above for 8 h. It was heat-dried at 110°C for 2 h and calcined at 500°C for 4 h. The catalyst thus prepared had a composition by weight of  $K_2MoO_4$  /  $Fe_2O_3$  /  $SiO_2$  = 0.5 / 0.03 / 1. See Table 1 for the activity assessment results.

Practical Example 2. The carrier used in Practical Example 1 was changed to  $TiO_2$ , while the remainder of the preparation method was the same as in Practical Example 1, and the composition and assessment results for the catalyst obtained are shown in Table 1.

Practical Example 3. 20 ml of distilled water was added to 0.58 ml of a 50% solution by weight of  $Mn(NO_3)_2$  to form a manganese nitrate solution, while the remainder of the method was as in Practical Example 1. The catalyst thus prepared had proportions by weight of  $K_2MoO_4$  /  $MnO_2$  /  $SiO_2$  = 0.5 / 0.025 / 1, and the activity assessment results are shown in Table 1.

Practical Examples 4-7. The "0.725 g of  $Fe(NO_3)_3 \cdot 9H_2O$ " in Practical Example 1 was changed to 1.16 g of  $Ni(NO_3)_2 \cdot 6H_2O$ , 1.16 g of  $Co(NO_3)_2 \cdot 6H_2O$ , 0.67 g of  $La(NO_3)_3$  and 0.66 g of  $Ce(NO_3)_3 \cdot 6H_2O$  respectively, while the remainder of the preparation was as in Practical Example 1. See Table 1 for the composition and activity assessment results of the catalysts obtained.

Table 1. Composition and Activity Assessment Results  
for the Catalysts in Practical Examples 1-7 \*

Practical Example	Catalyst composition (W) (active component Mo-O-K calculated as $K_2MoO_4$ )	$CH_3SH$ selectivity (%)	$CH_3SH$ space-time yield ( $g\ h^{-1}\ ml^{-1}\ cat$ )
1	$K_2MoO_4/Fe_2O_3/SiO_2 = 0.5/0.03/1$	98.6	0.33
2	$K_2MoO_4/MnO_2/SiO_2 = 0.5/0.03/1$	98.5	0.32
3	$K_2MoO_4/MnO_2/TiO_2 = 0.5/0.05/1$	92.7	0.29
4	$K_2MoO_4/NiO/SiO_2 = 0.5/0.03/1$	94.8	0.31
5	$K_2MoO_4/CoO/SiO_2 = 0.5/0.03/1$	98.6	0.32
6	$K_2MoO_4/La_2O_3/SiO_2 = 0.5/0.03/1$	98.6	0.32
7	$K_2MoO_4/CeO_2/SiO_2 = 0.5/0.03/1$	97.6	0.31

\* assessment conditions: high sulphur synthesis gas composition in proportions by volume of  $CO/H_2/H_2S = 1/2/1$ , reaction temperature  $295^\circ C$ , pressure 0.2 MPa, spatial velocity  $3 \times 10^3\ h^{-1}$ .

Practical Example 8. 0.725 g of  $Fe(NO_3)_3 \cdot 9H_2O$  was weighed out and dissolved in 20 ml of distilled water to make up a ferric nitrate solution, which was used to soak 10.0 g of  $SiO_2$  (grade 40-60) for 4 h, and this was heat-dried at  $110^\circ C$  for 2 h. It was then calcined in a muffle furnace at  $550^\circ C$  for 4 h ready for use. 2.67 g of  $K_2CO_3$  was weighed out and dissolved in 20 ml of distilled water. This was then used to soak the  $SiO_2$  carrier modified with iron as described above for 4 h, which was heat-dried at  $110^\circ C$  ready for use. 3.60 g of  $(NH_4)_6Mo_7O_{24}$  was weighed out and dissolved in 25 ml distilled water, which was used to soak the  $Fe_2O_3/SiO_2$  carrier modified with  $K_2CO_3$  for 8 h. It was heat-dried at  $110^\circ C$  and calcined at  $550^\circ C$  for 2 h. See Table 2 for the composition and activity assessment results of the catalyst obtained.

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Practical Example 9. The 2.67 g of  $K_2CO_3$  from Practical Example 8 was changed to 1.8 g of KOH, while the remainder of the preparation method was as in Practical

Example 8. See Table 2 for the composition and activity assessment results of the catalyst obtained.

5 Practical Example 10. The  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  in Practical Example 9 was changed to 3.0 g of  $\text{MoO}_3$ , while the remainder of the preparation method was as in Practical Example 8. See Table 2 for the composition and activity assessment results of the catalyst obtained.

10 Table 2. Composition and Activity Assessment Results for the Catalysts in Practical Examples 8-10 \*

Practical Example	Catalyst composition (W) (active component Mo-O-K calculated as $\text{MoO}_3/\text{K}_2\text{O}$ )	$\text{CH}_3\text{SH}$ selectivity (%)	$\text{CH}_3\text{SH}$ space-time yield ( $\text{g h}^{-1} \text{ml}^{-1} \text{cat}$ )
8	$\text{MoO}_3/\text{K}_2\text{O}/\text{Fe}_2\text{O}_3/\text{SiO}_2 = 0.3/0.15/0.03/1$	98.5	0.31
9	$\text{MoO}_3/\text{K}_2\text{O}/\text{Fe}_2\text{O}_3/\text{SiO}_2 = 0.3/0.15/0.03/1$	98.6	0.30
10	$\text{MoO}_3/\text{K}_2\text{O}/\text{Fe}_2\text{O}_3/\text{SiO}_2 = 0.3/0.15/0.03/1$	94.1	0.27


\* assessment conditions:  $\text{CO}/\text{H}_2/\text{H}_2\text{S} = 1/2/1$ , (V), 0.2 MPa,  $3 \times 10^3 \text{ h}^{-1}$ ,  $295^\circ\text{C}$ .

UNITED STATES PATENT AND TRADEMARK OFFICE

I, Charles Edward SITCH BA,

Managing Director of RWS Group Ltd UK Translation Division, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That the translator responsible for the attached translation is well acquainted with the Chinese and English languages.
3. That the attached is, to the best of RWS Group Ltd knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in China on October 10, 2003 under the number 2003101004961 and the official certificate attached thereto.
4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.

  
For and on behalf of RWS Group Ltd

The 7th day of July 2008

### Claims

1. Catalyst for the synthesis of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide, the said catalyst including a carrier and an active component, characterized in that the carrier is selected from silica, titanium oxide or a heavy rare earth oxide; the active component is a Mo-O-K based complex, its precursor being potassium molybdate (active component calculated as  $K_2MoO_4$ ) or ammonium molybdate plus a potassium salt or molybdenum oxide plus a potassium salt (active component calculated as  $MoO_3$  and  $K_2O$ ); when the active component is calculated as  $K_2MoO_4$ , the proportions by weight of the components in the catalyst are  $K_2MoO_4/\text{carrier} = (0.01-0.80)/1$ ; and when the active component is calculated as  $MoO_3$  and  $K_2O$ , the proportions by weight of the components in the catalyst are  $MoO_3/K_2O/\text{carrier} = (0.01-0.80)/(0.01-0.50)/1$ .

2. Catalyst for the synthesis of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide according to Claim 1, characterized in that when the active component is calculated as  $K_2MoO_4$ , the proportions by weight of the components in the catalyst are  $K_2MoO_4/\text{carrier} = (0.10-0.60)/1$ .

3. Catalyst for the synthesis of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide according to Claim 1, characterized in that when the active component is calculated as  $MoO_3$  and  $K_2O$ , the proportions by weight of the components in the catalyst are  $MoO_3/K_2O/\text{carrier} = (0.10-0.50)/(0.10-0.30)/1$ .

4. A method for preparing a catalyst for the synthesis of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide, characterized in that the steps are dissolving a measured amount of

the precursor of the Mo-O-K based complex active component in distilled water and soaking a measured amount of the selected carrier in this for 7-9 h, heat drying at 100-130°C and calcination at 400-500°C for 2-

5 4 h.

### Description

A Catalyst for the Synthesis of Methyl Mercaptan from  
Synthesis Gas Containing a High Concentration of  
Hydrogen Sulphide

#### (1) Technical Field

This invention relates to a supported catalyst for  
the single-step synthesis of methyl mercaptan ( $\text{CH}_3\text{SH}$ )  
from synthesis gas ( $\text{CO} + \text{H}_2$ ) containing a high  
concentration of  $\text{H}_2\text{S}$  as starting material and a method  
for its preparation.

#### (2) Prior Art

Methyl mercaptan is an important chemical engineering  
starting material for synthesizing protein amino acids,  
medical drugs and agrochemicals, and the traditional  
method for its manufacture is through the action of  
potassium hydrosulphide on a halogenated methane. Other  
synthesis routes have subsequently been developed, such  
as American patent US appl. 856,232, which disclosed a  
reaction of hydrogen sulphide with methanol or ethyl  
ether to form methyl mercaptan; French patent FR appl.  
93,112,491, which disclosed a method involving the  
hydrogenation of methylthioether for the preparation of  
methyl mercaptan using a transitional metal as  
catalyst; European patent EP 167,354, which disclosed a  
method for the preparation of methyl mercaptan using  
hydrogen sulphide and carbon monoxide as the starting  
material and with titanium oxide as the carrier and  
nickel oxide or molybdenum oxide as the active  
component. Chinese patents ZL 98118186.4 and  
ZL 98118187.2 disclosed a catalyst for the manufacture  
of methyl mercaptan from a synthesis gas containing a  
high concentration of  $\text{H}_2\text{S}$ , the active component being an  
Mo-S-K group produced by the conversion of a precursor  
 $\text{K}_2\text{MoS}_4$  or  $(\text{NH}_4)_2\text{MoS}_4$  plus a potassium salt. The space-

time yield of methyl mercaptan with this catalyst was relatively low ( $0.08-0.19 \text{ g}\cdot\text{h}^{-1}\cdot\text{ml}^{-1}_{\text{cat}}$ ), the preparation of the precursor was also very difficult, and water could not be used as the carrier solvent, requiring the use of DMF, so that the manufacturing cost of the catalyst was high.

### (3) Scope of Invention

The objective of this invention is to provide a catalyst for the single-step preparation of methyl mercaptan from synthesis gas containing a high concentration of hydrogen sulphide as starting material and which features cheap starting materials, simple preparation, a high methyl mercaptan space-time yield and relatively high activity and selectivity.

The said catalyst of this invention includes a carrier and an active component, with the carrier selected from silica ( $\text{SiO}_2$ ), titanium oxide ( $\text{TiO}_2$ ) or a heavy rare earth oxide; the active component is a Mo-O-K based complex, its precursor being potassium molybdate (active component calculated as  $\text{K}_2\text{MoO}_4$ ) or ammonium molybdate  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}]$  plus a potassium salt or molybdenum oxide ( $\text{MoO}_3$ ) plus a potassium salt (active component calculated as  $\text{MoO}_3$  and  $\text{K}_2\text{O}$ ); when the active component is calculated as  $\text{K}_2\text{MoO}_4$ , the proportions by weight of the components in the catalyst are  $\text{K}_2\text{MoO}_4/\text{carrier} = (0.01-0.80)/1$  and preferably  $(0.10-0.60)/1$ ; and if the active component is calculated as  $\text{MoO}_3$  and  $\text{K}_2\text{O}$ , the proportions by weight of the components in the catalyst are  $\text{MoO}_3/\text{K}_2\text{O}/\text{carrier} = (0.01-0.80)/(0.01-0.50)/1$  and preferably  $(0.10-0.50)/(0.10-0.30)/1$ .

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The method for preparing the catalyst is: a measured amount of the precursor of the Mo-O-K based complex active component is dissolved in distilled water, and a measured amount of the selected carrier is soaked in

this for 7-9 h, heat dried at 100-130°C and calcined at 400-500°C for 2-4 h.

Assessment of catalyst activity is carried out in a fluid reaction system on a fixed bed, with the composition of the synthesis gas containing a high concentration of  $H_2S$  being (proportions by volume)  $CO/H_2/H_2S = 1/2/(0.1-1)$ , reaction temperature 220-350°C, pressure 0.2-2.0 MPa, spatial velocity  $(2-5) \times 10^3 \text{ h}^{-1}$ . The compositions of the starting material gas and product are determined by gas chromatography. The catalyst is first reduced for 8 h by  $H_2$  at 300-350°C, after which starting material gas is passed in for 8 h followed by measurement of product composition.

As is generally known, the properties and performance of a catalyst are determined by the starting materials for its manufacture and the manufacturing method (including process conditions). When the catalyst contains a certain element, for example Mo, it is in principle possible to select all simple substances or compounds containing the element Mo as one of the starting materials for manufacture of this catalyst. However, different starting materials inevitably introduce other different groups or atoms, so that when selecting  $MoO_3$ , O atoms are introduced, while when selecting ammonium molybdate, O atoms and  $NH_4^+$  groups are introduced. These other introduced groups will affect the physical changes and chemical changes which occur during the catalyst manufacturing process, and thus finally result in differences in the properties and performance of the catalyst. This invention prepares a catalyst with high activity and selectivity through the selection of appropriate starting materials containing Mo and K, and under the assessment conditions of this invention, the space-time yield of methyl mercaptan was  $0.25 \text{ g} \cdot \text{h}^{-1} \cdot \text{ml}^{-1}_{\text{cat}}$ , and selectivity reached 98.8%. Furthermore, the selected starting

materials are cheap and readily obtainable, and the manufacturing process is simple and convenient.

#### (4) Embodiments

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This invention is further described below by means of practical examples.

10 Practical Example 1. 1.0 g of  $K_2MoO_4$  was weighed out and dissolved in 5 ml of distilled water. 2 g of  $SiO_2$  (grade 40-60) was soaked in this for 8 h, heat dried at  $110^\circ C$  for 2 h and calcined at  $500^\circ C$  for 2 h. The proportions by weight of the components in the catalyst thus prepared were  $K_2MoO_4/SiO_2 = 0.50/1$ , and the activity  
15 assessment results are shown in Table 1.

Practical Examples 2 and 3. The carrier  $SiO_2$  in Practical Example 1 was changed to  $TiO_2$  or a heavy rare earth oxide, with the remainder of the preparation  
20 method as in Practical Example 1. The activity assessment results are shown in Table 1.

Practical Example 4. 0.72 g of  $(NH_4)_6Mo_7O_{24}$  and 0.88 g of  $K_2CO_3$  were weighed out and dissolved in 5 ml of  
25 distilled water. 2 g of  $SiO_2$  carrier was soaked in this for 8 h, heat dried at  $110^\circ C$  and calcined at  $450^\circ C$ . The proportions by weight of the components in the catalyst prepared from this were  $MoO_3/K_2O/SiO_2 = 0.30/0.30/1.0$ , and its activity assessment results are shown in Table  
30 1.

Practical Example 5. 0.44 g of  $K_2CO_3$  was weighed out and dissolved in 5 ml of distilled water. 2 g of  $SiO_2$  was soaked in this for 4 h and heat dried at  $110^\circ C$ . 0.72 g  
35 of  $(NH_4)_6Mo_7O_{24}$  was weighed out and dissolved in 5 ml of distilled water, and the  $SiO_2$  carrier which had been modified by  $K_2CO_3$  was soaked in this for 8 h, heat dried at  $110^\circ C$  and calcined at  $450^\circ C$  for 2 h. The proportions by weight of the components in the catalyst thus

prepared were  $\text{MoO}_3/\text{K}_2\text{O}/\text{SiO}_2 = 0.30/0.15/1$ , and the activity assessment results are shown in Table 1.

Practical Example 6. The 0.44 g of  $\text{K}_2\text{CO}_3$  in Practical Example 5 was changed to 0.36 g of KOH, while the remainder of the preparation method was as in Practical Example 5. The proportions by weight of the components in the catalyst prepared were  $\text{MoO}_3/\text{K}_2\text{O}/\text{SiO}_2 = 0.30/0.15/1$ . The activity assessment results are shown in Table 1.

Practical Example 7. 0.6 g of  $\text{MoO}_3$  and 0.36 g of KOH were weighed out and dissolved in 5 ml of distilled water. 2 g of  $\text{TiO}_2$  (grade 40-60) carrier was soaked in this for 8 h, heat dried at  $110^\circ\text{C}$  and calcined at  $450^\circ\text{C}$  for 2 h. The proportions by weight of the components in the catalyst prepared were  $\text{MoO}_3/\text{K}_2\text{O}/\text{TiO}_2 = 0.30/0.15/1$ . The catalyst activity assessment results are shown in Table 1.

Table 1. Composition and Activity Assessment Results for the Catalysts in Practical Examples 1-7 \*

Practical Example	Catalyst composition (proportions by weight) %	$\text{CH}_3\text{SH}$ selectivity (%)	$\text{CH}_3\text{SH}$ space-time yield ( $\text{gh}^{-1}\text{ml}^{-1}_{\text{cat}}$ )
1	$\text{K}_2\text{MoO}_4/\text{SiO}_2 = 0.5/1$	98.5	0.25
2	$\text{K}_2\text{MoO}_4/\text{TiO}_2 = 0.5/1$	98.8	0.24
3	$\text{K}_2\text{MoO}_4/\text{heavy rare earth} = 0.5/1$	98.8	0.24
4	$\text{MoO}_3/\text{K}_2\text{O}/\text{SiO}_2 = 0.30/0.30/1$	96.8	0.23
5	$\text{MoO}_3/\text{K}_2\text{O}/\text{SiO}_2 = 0.30/0.15/1$	97.2	0.24
6	$\text{MoO}_3/\text{K}_2\text{O}/\text{SiO}_2 = 0.30/0.15/1$	94.2	0.21
7	$\text{MoO}_3/\text{K}_2\text{O}/\text{TiO}_2 = 0.30/0.15/1$	93.5	0.18

\* assessment conditions:  $\text{CO}/\text{H}_2/\text{H}_2\text{S} = 1/2/1$ , (V), 0.2 MPa,  $295^\circ\text{C}$ ,  $3 \times 10^3 \text{ h}^{-1}$ .